

DEVELOPMENT AND OPTIMIZATION OF ZEOLITE SYNTHESIS ROUTE  
FROM NATURAL KAOLIN FOR ADSORPTION OF DYES

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*This thesis is dedicated to all students that have lost their lives in the path of seeking knowledge. May Allah accept your Shahadah.*



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## ABSTRACT

Synthesis of zeolite using kaolin as the main source of alumina and silica has been identified as a novel zeolite production process, which could reduce the cost of using the synthetic reagents and the high energy consumption. A low grade kaolin was used for studying the most suitable synthesis route and operating parameters for producing a high yield and pure phase zeolite. The study adopted the alkaline activation and microwave assisted heating as modification techniques of the conventional hydrothermal synthesis process. Calcination and crystallization processes were identified as the bottleneck operations within the process. Hence, this study employed  $2^k$  factorial design of experiment to study the relationship of metakaolinization temperature of 600 – 800 °C with calcination time of 1 – 5 hours. And that of crystallization time of 9 – 16 hours with aging treatment time of 12 – 36 hours. Central Composite Design (CCD) is used for optimization with axial and center point for factors evaluation towards the responses; yield percent (%) and crystallinity (%) for crystallization process. Based on the Response Surface Methodology (RSM), with desirability value of 98.67 %, the significant parametric aging condition is 27 hours and crystallization time is 9 hours were suggested to yield an optimum product for 80.47 yield percent and 76.92 crystallinity. Three confirmation runs were performed based on the suggested optimum parameter and the calculated error value was found to be below 10 %. The synthesized zeolite-A from the confirmation runs was characterized through XRD. The results were then corroborated with the analytical results from SEM, BET and FTIR. The activity of the synthesized zeolite A was confirmed by a structural refinement analysis, that identified the product as a member of the cubic crystalline systems, belonging to a Fm3c space group with lattice cubic structure values where:  $a = b = c = 24.58 \text{ \AA}$ . The synthesized zeolite-A was compared favorably against other low cost adsorbents through its ability to adsorb 2.44 mg/g methylene blue dye at a very low adsorbent medium of 1.5 g/L. The mathematical models suggested by RSM therefore, adequately described the crystallization responses within the zone factors being investigated. It is an outstanding finding to obtain zeolite A, having more than 76% crystallinity, 96.6% phase purity and yielding above 80% from a low grade kaolin and at a considerable low temperature of 90 °C and 9 hours crystallization time, without applying any synthetic reagent, as compared to the previous studies that involved the use of expensive and harmful reagents and Structural Directing Agents (SDA) which required longer time and high temperature for crystallization and for post treatment.

## ABSTRAK

Sintesis zeolit menggunakan kaolin sebagai sumber utama alumina dan silika telah dikenal pasti sebagai proses pengeluaran zeolit novel, yang dapat mengurangkan kos penggunaan reagen sintetik dan penggunaan tenaga yang tinggi. Kaolin gred rendah telah digunakan untuk mengkaji laluan sintesis zeolite yang paling sesuai dan parameter operasi yang sesuai bagi mendapatkan zeolite dengan hasil yang banyak dan berketulenan tinggi. Kajian ini mengadaptasi pengaktifan alkali dan pemanasan gelombang mikro sebagai teknik pengubahsuaian kepada proses sintesis hidroterma konvensional. Proses pengkalsinan dan penghabluran dikenalpasti sebagai operasi penentuan dalam proses tersebut. Oleh itu, kajian ini menggunakan reka bentuk ujikaji faktorik 2k untuk mengkaji interaksi suhu metakaolinisasi 600-800 oC dengan masa pengkalsinan di antara 1-5 jam, masa penghabluran 9-16 jam dengan tempoh pematangan 12-36 jam. Reka bentuk Komposit Sentral digunakan untuk pemodelan dengan titik paksi dan pusat untuk penilaian faktor terhadap respons; peratusan hasil (%) dan penghabluran (%) untuk proses penghabluran. Berdasarkan kaedah permukaan gerak balas (RSM), dengan nilai keinginan 98.67%, keadaan pematangan parametrik yang signifikan ialah 27 jam dan masa penghabluran ialah 9 jam telah dicadangkan untuk menghasilkan produk optimum bagi 80.47 % peratus hasil dan 76.91 % penghabluran. Pengesahan dijalankan sebanyak tiga kali berdasarkan parameter optimum yang disyorkan dan nilai pengiraan kesalahan yang dikira didapati berada di bawah 10 %. Zeolit-A yang disintesis daripada pengujian pengesahan telah dicirikan dan disahkan melalui XRD. Hasilnya disokong dengan hasil analisis dari SEM, BET dan FTIR. Penghasilan sintesis zeolit A yang telah disahkan oleh analisis penyempurnaan struktur, telah dikenalpasti dari ahli sistem hablur kubik, yang dipunyai oleh kumpulan ruang Fm3c dengan struktur nilai kekisi di mana:  $a = b = c = 24.58 \text{ \AA}$ . Zeolit-A yang disintesis adalah lebih baik berbanding jenama komersil di pasaran berdasarkan keupayaannya untuk menyerap sebanyak 2.44 mg/g pewarna methalena biru (MB) dengan kuantiti medium bahan serapan yang sangat rendah sebanyak 1.5 g/L. Oleh itu, matematik model yang dicadangkan oleh RSM, secara tepatnya menunjukkan respon penghabluran berada di zon faktor yang dikaji. Ia adalah satu penemuan yang cemerlang untuk mendapatkan zeolit A, mempunyai lebih daripada 76 % penghabluran, fasa ketulenan 96.6 % dan hasil yang melebihi 80 % dari kaolin gred rendah pada suhu yang dikira agak rendah iaitu 90 oC dan masa penghabluran iaitu 9 jam, tanpa menggunakan apa-apa bahan tindakbalas sintetik berbanding dengan kajian sebelumnya yang melibatkan penggunaan bahan mahal dan berbahaya dan SDA yang memerlukan masa yang lebih lama dan suhu tinggi untuk penghabluran dan rawatan lanjutan.

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## LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
ASTM	-	American society for testing and materials
BET		Brunauer–Emmett–Teller
DF	-	Degree of freedom
DGS	-	Dry gel conversion
DOE	-	Design of experiment
ED	-	Electro dialysis
FAU	-	Faujite topology
FTIR	-	Fourier-transform infrared Spectroscopy
GIS	-	Gismodine
ICDD	-	International centre for diffraction data
ICSD	-	Inorganic Crystal Structure Database.
IZA	-	International zeolite association
LOI	-	Loss on ignition
LTA	-	Linde type Alpha
MB	-	Methylene blue
MED	-	Multiple effect distillation
MOR	-	Mordenite topology
MO	-	Methyl orange
MSF	-	Multi-stage flash distillation
Mt	-	Million ton
O	-	Oxygen
PBU	-	Primary building unit
PRESS	-	Predicted residual error sum of squares
R <sup>2</sup>	-	Coefficient of determination
RO	-	Reverse osmosis

RSM	-	Response surface methodology
SAC	-	Steam-assisted crystallization
SBU	-	Secondary building unit
SDA	-	Structural directing agent
SEM	-	Scanning electron microscopy
SOD	-	Sodalite
T	-	Tetrahedral
TEOS	-	Tetraethylorthosilicate
TGA	-	Thermogravimetric analyzer
UTHM	-	Universiti Tun Hussien Onn Malaysia
VCD	-	Vapor compression distillation
VPT	-	Vapor-phase transport
XRD	-	X-ray diffraction
XRF	-	X-ray fluorescence



PTTA UTHM  
PERPUSTAKAAN TUNKU TUN AMINAH

## LIST OF EQUATIONS

- 2.1 - Structural formula of zeolite
- 2.2 - Sodium ion exchange in the zeolite framework
- 2.3 - Transformation of kaolin to metakaolin
- 2.4 - Transformation of hydroxyl groups into water molecules
- 2.5 - Quadratic model for predicting the optimal conditions
- 2.6 - Simultaneous desirability objective function
- 2.7 - Chemical reactions of adsorption on a single layer
- 2.8 - Langmuir adsorption isotherm
- 2.9 - Langmuir adsorption isotherm
- 2.10 - Factor constants for non-dimensional separation
- 2.11 - Freundlich isotherm adsorption model
- 2.12 - Freundlich isotherm adsorption model by logarithm
- 2.13 - Kinetic reaction equation
- 2.14 - Pseudo-first-order reaction model
- 2.15 - Straight line equation pseudo-first-order reaction model
- 2.16 - Pseudo-second-order reaction model
- 2.17 - Pseudo-second-order reaction model equation of linearity
- 2.18 - Intra-particle diffusion
- 3.1 - MB Removal efficiency
- 3.2 - Adsorption capacity at equilibrium
- 3.3 - Adsorption capacity at any time
- 3.4 - Loss on ignition
- 3.5 - Beer-Lambert Laws
- 3.6 - BET-sample weight
- 4.1 - Final quadratic model for weight loss
- 4.2 - Final quadratic model for peak intensity

- 4.3 - Percentage error
- 4.4 - Final quadratic model for yield percent purity
- 4.5 - Final quadratic model for crystallinity





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